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⑤④ Process for producing polymaleate.

⑤⑦ A polymaleate having an average molecular weight of  
300 to 5000 is obtained by polymerizing a monoalkali metal  
maleate or monoammonium maleate at 80 to 180°C in the  
presence of a polymerization initiator in an aqueous sol-  
vent.

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# PROCESS FOR PRODUCING POLYMALEATE

The present invention relates to a process for producing a polymaleate. More particularly, the invention relates to a process for producing a polymaleate having an average molecular weight in a specified range in an aqueous solvent with a high efficiency.

Polymaleic acid and copolymers of maleic acid with other monomers have been used as a dispersing agent and scale inhibitor. The polymaleic acid has been prepared in the prior art by using a peroxide such as benzoyl peroxide as a polymerization initiator in an organic solvent such as toluene or xylene. However, from the industrial viewpoint, an aqueous solvent is far preferred to an organic solvent in



the production of the polymaleic acid in view of simplification of the production steps, reduction of the cost and prevention of fire hazard. Nevertheless, there can hardly be found reports of the polymerization of maleate in an aqueous solvent. Only reports relating to copolymers of maleic acid with acrylic acid or vinyl acetate are found.

After intensive investigations of the polymerization reaction of maleates in an aqueous medium carried out under these circumstances, the inventors have found that a polymaleate having an average molecular weight of 300 to 5000 can be produced efficiently by using a monoalkali metal maleate or monoammonium maleate as the monomer. The present invention has been completed on the basis of this finding. The present invention provides a process for producing a polymaleate having an average molecular weight of 300 to 5000 characterized by polymerizing a monoalkali metal maleate or monoammonium maleate at 80 to 180°C in the presence of a polymerization initiator in an aqueous solvent.

The process of the present invention will now be described in detail. First, an aqueous solution of maleic acid or maleic anhydride is prepared. Then, an aqueous solution of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide or



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aqueous ammonia is added to the solution in a quantity equimolar to maleic acid or maleic anhydride or a quantity excess by up to 10 molar % to obtain an aqueous solution of a monoalkali metal maleate or monoammonium maleate having a pH of 3.5 to 5.0. A polymerization initiator preferably in an amount of 0.02 to 0.6 mol, particularly 0.05 to 0.4 mol, per mol of the monomer, is added to the aqueous solution at once or in portions. The polymerization is carried out at 80 to 180°C, preferably 100 to 150°C.

The concentration of the aqueous solution of the monoalkali metal maleate or monoammonium maleate used in the process of the present invention is not particularly limited. However, a solid concentration of 30 to 60 wt.% is practically preferred. Though the polymerization reaction time is not particularly limited as well, it is preferably at least 3 h, particularly 4 to 10 h.

As the polymerization initiator used for the polymerization reaction, there may be mentioned hydroperoxides such as t-butyl hydroperoxide or cumene hydroperoxide; dialkyl peroxides such as di-t-butyl peroxide; persulfates such as ammonium persulfate; redox initiators such as persulfate/sulfite; and water-soluble azobis compounds.



According to the process of the present invention, polymaleates having an average molecular weight of 300 to 5000 can be obtained efficiently and easily. Though the mechanism has not been elucidated yet, it is considered that the monoalkali metal maleate or monoammonium maleate forms an intramolecular hydrogen bond in the aqueous solution to realize a planar structure, whereby the radical resonance stabilization is enhanced and the polymerizability is improved.

In the process of the present invention, up to 20 molar %, based on the maleate, of an unsaturated carboxylic acid such as acrylic acid, methacrylic acid or itaconic acid; an acrylic derivative such as an acrylamide, (meth)acrylate or hydroxy(meth)acrylate; or an unsaturated sulfonic acid such as styrenesulfonic acid or allylsulfonic acid may be added to the reaction system to produce the copolymer of the maleate with the unsaturated compound efficiently.

The polymaleates produced by the process of the present invention have particularly excellent dispersing capacity and calcium ion-uptaking capacity and they can be used as a scaling inhibitor, pigment dispersant or builder for a detergent.

The following examples will further illustrate



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the present invention, which by no means limit the invention.

#### Example 1

102g (1.224 mol as pure sodium hydroxide) of 48% aqueous sodium hydroxide solution was added to an aqueous solution containing 117.6g (1.2 mol) of maleic anhydride to obtain 50 wt.% aqueous solution of monosodium maleate. The whole quantity of the aqueous solution was transferred into a 500 ml autoclave. Nitrogen was introduced therein under stirring and the temperature of the reaction system was elevated to 90°C. 10.13g (8.104g as pure t-butyl peroxide) of 80% t-butyl peroxide (molecular weight: 90) was introduced into the reaction system as a polymerization initiator through a sample-inlet tube. Thereafter, the introduction of nitrogen was stopped. The autoclave was closed and the temperature was elevated to 130°C. The stirring was continued at that temperature for 2 h and the reaction system was cooled to 90°C. At this time, the aqueous solution had a pH of 5.2 and a concentration of 3%. Hydrochloric acid was added to the mixture through another sample-inlet pipe to control the pH of the 3% aqueous solution to 4.1, since a pH in the range of 3.5 to 5.0 is preferred for accelerating the reaction. Additional

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10.13g of 80% t-butyl hydroperoxide was introduced in the reaction system through the sample-inlet tube. The autoclave was closed and the temperature was elevated to 130°C. The stirring was effected at this temperature for 1.5 h. Then, the reaction system was cooled to 90°C. 5.4g of 80% t-butyl hydroperoxide was added to the mixture. The pH of the 3% aqueous solution was controlled to 4.12 with hydrochloric acid. The temperature was elevated to 130°C and the mixture was stirred at this temperature for 1.5 h to complete the reaction. The quantity of the polymerization initiator was about 0.23 mol per mol of maleic anhydride. A filter aid (trade name: Radiolite #900) was added to the reaction mixture to effect filtration through a glass filter and obtain 3% aqueous solution of monosodium polymaleate having a solid content of 43% and a pH of 4.4. The polymerization rate was determined from the results of determination of maleic acid residue according to the bromine/bromide method.

For comparison, a polymaleate was prepared in the same manner as above except that the quantity of sodium hydroxide used for the neutralization of the initial 50 wt.% aqueous maleate solution was varied. The average molecular weights of the

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resulting polymer salts and polymerization rates are shown in Table 1.

Table 1

Run No.	Degree of neutralization of maleic acid (molar ratio of maleic acid/NaOH)	Final pH	Polymerization rate (molar %)	Average molecular weight *1
1	1.00 / 1.02	4.4	92.8	550
2	1.00 / 2.00	11.0	64.0	-
3	1.00 / 0.75	3.1	49.2	-

Run No. 1 : example of the present invention

Run Nos. 2 and 3 : comparative examples

In the comparative examples, the average molecular weights were not determined, since the polymerization rates were low.

The reaction in Run No. 2 was a polymerization reaction using disodium maleate. The reaction in Run No. 3 was a copolymerization reaction using a mixture of monosodium maleate and maleic acid.

\*1 Average molecular weight: The sodium salt of the polymer was diluted to 500 mg/100 ml (as solid) with deionized water. A 100  $\mu$ l portion of the solution was taken and number-average molecular weight was determined according to gel permeation chromatography in a 0.15 M phosphate buffer





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solution (pH 7.0) using an aqueous column G 4000PW/G2000SW (a product of Toyo Soda Co., Ltd.) at room temperature. Light absorption at 215 nm was determined by means of Spectrophotometric detector SPD-1 (a product of Shimadzu Seisaku-Sho Co., Ltd.). In the following examples, the average molecular weights were determined in the same manner as above.

#### Example 2

The same procedure as in Experiment No. 1 in Example 1 was repeated except that the concentration of monosodium maleate in the aqueous solution was varied. The results are shown in Table 2.

Table 2

Experiment No.	Conc. of monosodium maleate (wt.%)	Polymerization rate (molar %)	Average molecular weight
4	40	90.8	480
5	30	84.5	420

#### Example 3

The whole quantity of 50 wt.% aqueous solution of monosodium maleate prepared in the same manner as in Example 1 was charged in a 500 ml autoclave. The temperature of the reaction system was elevated to

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## Example 4

An aqueous solution of 198 g (2.0 mol) of maleic anhydride was introduced into a one liter, four-necked flask provided with a stirrer, a tap funnel and a reflux condenser and then 170 g of a 48 % aqueous caustic soda solution was added thereto in order to prepare a 50 % aqueous solution of monosodium maleate. A pH value of the obtained solution was 4.1 at a concentration of 3 %. The aqueous solution was heated up to 100°C while agitated. After that, a solution obtained by dissolving 23.8 g of sodium persulfate in 150 g of 35 % aqueous hydrogen peroxide was added dropwise over a period of 5 hours with a tap funnel. Thereafter the mixture was stirred at 100°C for further 2 hours in order to complete the reaction. Then the aqueous solution was cooled down to a room temperature and filterated with a glass filter with a filter assistant a tradename of which was Radiorite #900. In this way, an aqueous solution of monosodium polymaleate having a solid content of 39 %. A pH value of the solution was 5.2 at a concentration of 3 %.

A polymerization rate of the example was measured based on quantitative determination of remaining maleic acid according to the bromine/bromide method. Results are shown in Table 4.



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90°C. 22g of 80% cumene hydroperoxide (molecular weight: 152) as a polymerization initiator was introduced in the reaction system through a sample-inlet tube. The mixture was stirred at 130°C for 2 h and then cooled to 90°C. The pH of the 3% aqueous solution was controlled to 4.2 with hydrochloric acid. Additional 22g of 80% cumene hydroperoxide was added to the mixture. After stirring at 130°C for 2 h, the reaction system was cooled to 90°C. Additional 10g of 80% cumene hydroperoxide was added to the mixture and stirring was continued at 130°C for 1 h to complete the reaction. The quantity of the polymerization initiator was about 0.24 mol per mol of maleic anhydride. The solvent for cumene hydroperoxide was stripped under vacuum. Water was added to the resulting residue to obtain an aqueous sodium polymaleate solution having a solid content of 40 wt.%. The results are shown in Table 3.

Table 3

Experiment No.	Degree of neutralization of maleic acid (molar ratio of maleic acid/NaOH)	Final pH	Polymerization rate (molar %)	Average molecular weight
6	1.00 / 1.02	4.35	91.1	610

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Table 4

Run No.	degree of neutralization of maleic acid (molar ratio of maleic acid to NaOH)	final pH	polymerization rate (mole %)	average molecular weight
7	1.00/1.02	5.2	92.2	690

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What is claimed is:

1. A process for producing a polymaleate having an average molecular weight of 300 to 5000 characterized by polymerizing a monoalkali metal maleate or monoammonium maleate at 80 to 180°C in the presence of a polymerization initiator in an aqueous solvent.
2. A process as claimed in Claim 1, in which said monoalkali metal maleate or monoammonium maleate is used in an aqueous solution obtained by adding an aqueous solution of an alkali metal hydroxide or an aqueous ammonium to an aqueous solution of maleic acid or maleic anhydride in an equimolar amount or in a 10 percent excess, having a pH value of 3.5 to 5.0.
3. A process as claimed in Claim 1 or 2, in which the alkali metal is sodium or potassium.
4. A process as claimed in one of Claims 1 to 3, in which hydroperoxides, dialkylperoxides, persulfates, redox initiators or water soluble azobis compounds are used as initiators in an amount of 0.02 to 0.6 mol per mol of the monomer.

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# EUROPEAN SEARCH REPORT

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Application number

EP 83 10 9893

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	GB-A- 597 590 (BECK, KOLLER AND COMPANY) * Claim 1; example 4 *  -----	1-3	C 08 F 22/02 C 08 F 2/10
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06-02-1984	Examiner CAUWENBERG C. L. M.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	

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